

THERMODYNAMIC EFFICIENCY OF COGENERATION OF ELECTRICAL ENERGY AND HYDROGEN IN GAS-TURBINE CYCLE OF METHANE OXIDATION

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UDC 536.755:621.43.018

Two of the most urgent problems in large-scale energetics are how to improve the efficiency of utilization of natural gas, which will be the most important primary source of energy in the next decade, and how to avoid the atmospheric discharges of carbon dioxide that are responsible for global warming [1].

The main avenues of loss of chemical exergy of methane in existing power units are the resistance to heat transfer from the flue gas to the working medium of the turbine and the irreversibility of the combustion itself. The first avenue of loss is eliminated in a gas-turbine cycle with internal combustion of methane. In this article we will examine the feasibility of achieving a substantial lowering of the irreversibility of combustion through the combined conversion of methane in a gas-turbine cycle to electrical energy and hydrogen.

It had already been noted [2] that the equilibrium temperatures of combustion of the products from steam and carbon dioxide conversion of methane — H_2 and CO — are incomparably lower than the characteristic combustion temperature of methane itself; i.e., the combustion of converted gas is less of a nonequilibrium process. Direct calculations show that the difference between the magnitude of entropy production in these two reactions increases appreciably with increasing temperature and increasing concentrations of the combustion products — water and carbon dioxide. Such effects could be used to improve the thermodynamic efficiency of power units in a closed gas-turbine cycle with intermediate conversion of methane under the influence of the combustion products. The desirability of maintaining a significant excess of H_2O and CO_2 , both in the stage of converted gas combustion and in the stage of the methane conversion reaction (in order to ensure a high yield of the latter stage), suggests that the air that is traditionally used in gas-turbine units as the oxidizing agent should be replaced by pure oxygen, fed to the combustion chamber in a stoichiometric amount relative to the fuel. Of course, in order to balance the exothermic and endothermic chemical processes in the cycle, it will be advisable to withdraw from the system, through selective membranes, part of the hydrogen that is formed (or part of the mixture of hydrogen and carbon monoxide). An illustrative scheme of the cycle is shown in Fig. 1.

In order to clarify the thermodynamic effect of cogeneration of hydrogen and electrical energy in the cycle, we have taken as a standard a hypothetical cycle of direct oxidation of methane, also by pure oxygen. The selection of the points of methane introduction and combustion product withdrawal in the cycle (Fig. 1) is dictated specifically in the present case by considerations of a continuous transition from a complex cycle to the standard cycle (successive removal of modules 8 and 5) with identical p and T for the streams of methane and combustion products. In the flow plan, the membrane module is placed after the compressor, in order to have the withdrawn hydrogen at higher pressures. Optimization of the positions of the points at which the streams are introduced and withdrawn requires a concrete definition of the entire structure of the gas-turbine unit, including its auxiliary elements.

The conversions taking place in the system are described by the overall equation



where x is the number of moles of hydrogen withdrawn per mole of methane. The limiting value of x is determined by the degree of methane conversion in the reactor, and it cannot be greater than 2.

In the analysis, attention was focused mainly on constructing a trajectory of chemical conversion of the fuel that is closest to an equilibrium trajectory; therefore, all of the accompanying thermomechanical processes in the cycle (compression,

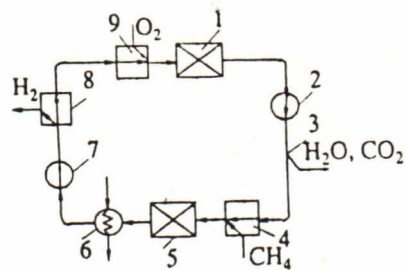


Fig. 1. Flow plan of gas-turbine cycle with intermediate conversion of methane and withdrawal of hydrogen: 1) fuel combustion; 2) expansion in turbine; 3) withdrawal of combustion product; 4) introduction of methane; 5) conversion of methane; 6) heat exchanger; 7) compression in compressor; 8) withdrawal of hydrogen through ~~membrane~~ *membrane*; 9) introduction of oxygen.

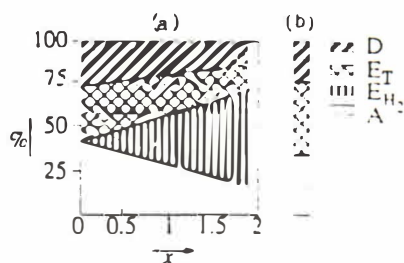


Fig. 2. Transformation of exergy of fuel to electrical energy, exergy of hydrogen, and thermomechanical exergy in cycle with intermediate conversion of methane, depending on amount of hydrogen taken off (a), and in cycle of direct methane oxidation (b).

expansion, heat exchange, transfer of gas mixture) were assumed to be quasireversible. Correspondingly, the pressures and temperatures of the streams being mixed were considered to be identical. The only processes that were considered to be nonequilibrium were autothermal processes of combustion and conversion, transport of hydrogen through the membrane, and mixing of components (operations 4 and 9). Also, it was assumed that complete oxidation of the fuel takes place in the combustion chamber. Finally, it was assumed that the area of the contact catalytic surface of the converter was sufficiently large that equilibrium temperatures could be reached, as well as an equilibrium composition of the mixture at the converter outlet, and that the permeable area of the selective membrane was sufficiently large that the residual partial pressure of hydrogen in the circulating stream would be reduced at the outlet of the membrane module all the way to equilibrium with the pressure of the hydrogen drawn off (after the membrane). These assumptions, which eliminate the need for defining specifically the process kinetics, do not distort the relative contributions of the various components of the exergy loss.

The exergy loss was calculated as $D_i = T_0 \Delta S_i$ ($i = 1, 4, 5, 8, 9$), where $T_0 = 298$ K; ΔS_i is the difference of entropies of the flows at the inlet and outlet of the i th module. In Table 1 we present the results of sample calculations for specific values of the maximum temperature of the cycle (temperature of the gas fed to the turbine) $T_{\max} = 1473$ K, maximum and minimum pressures $p_{\max} = 10$ atm and $p_{\min} = 1$ atm, and also the ratio of flow of the gas mixture through the turbine (in moles) to the methane feed flow 30:1. In Fig. 2 we show the basic output characteristics of the cycles: A is the work taken off; E_{H_2} is the chemical exergy of the hydrogen produced; E_T is the total thermomechanical exergy of the material streams that are withdrawn, including hydrogen, and the heat taken from the heat exchanger 6; D is the total loss of exergy, expressed as a percentage of the total exergy of the flows at the inlet E_0 (this is mainly the chemical exergy of methane $E_{CH_4} 818.1$ kJ/mole). Also, we have indicated separately in Table 1 the exergy withdrawn from the heat cycle E_Q and the thermomechanical exergy of the material streams that are withdrawn $E_T - E_Q$, and also the desired efficiency (based on the total generation of electrical energy and hydrogen) and the exergetic efficiency of the cycles $\eta = (A + xE_{H_2})/E_{CH_4}$ and $\eta_c = (E_0 - D)/E_0$. In view of the assumptions that have been made, the latter expression represents the internal efficiency of the cycles.

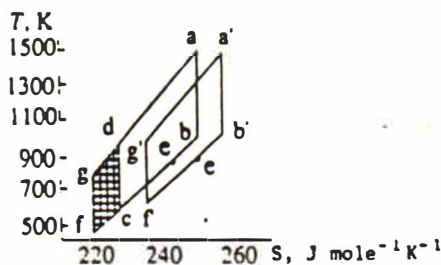


Fig. 3. Change of state of working medium in cycles with direct oxidation of CH_4 ($abcda$), with oxidation of conversion products without takeoff of hydrogen ($abefga$), and with takeoff of hydrogen, $x = 1$ ($a'b'e'f'g'a'$).

TABLE I

Cycle*	x	D_1^{**}	D_2	D_3	$D_4 + D_n$	E_n	E_0	$E_T - E_0$	η	η_e
1	-	179	-	-	29	867	301	54	0.37	0.76
2	0	172	24	-	29	860	226	54	0.43	0.74
	0.5	135	24	0.1	28	862	207	48	0.51	0.78
	1	104	25	0.5	26	862	180	44	0.59	0.82
	1.5	78	27	2.1	24	862	144	39	0.67	0.85

*Cycle 1 is direct oxidation of CH_4 ; cycle 2 is the cycle with intermediate conversion of CH_4 .

**Absolute values of exergy are expressed in kJ per mole of methane consumed.

It is more convenient to give a thermodynamic interpretation ^{of the} results on a T-S diagram constructed for the main working substance (present in large excess) that is circulating in the loop — a mixture of H_2O and CO_2 with a stoichiometric composition corresponding to overall conversion of methane in accordance with Eq. (1). The change of state of the working substance takes place in a closed Brighton adiabat-isobaric cycle (Fig. 3). Here, for example, the isobar ga for the second variant of the cycle corresponds to heating of the working substance as a result of fuel combustion; the other isobar bf includes two sections be and ef corresponding to cooling of the working substance as a result of the conversion reaction and in the heat exchanger 6. Thus, we actually show on the diagram the change of T in all sections of the cycle, calculated with allowance for all of the changes taking place in the chemical composition of the circulating mixture, as well as the accompanying change of entropy of the principal working substance $S(T)$. As can be seen from Fig. 3, in the cycle with intermediate conversion, the work (area of the cycle) is greater in magnitude in comparison with the work in the direct oxidation of CH_4 , as a consequence of the reduction of exergy of the heat withdrawn in the heat exchanger (in the interval ef , instead of bc), the decrease in magnitude of the work of the compressor, and the corresponding increase of heat evolution in the combustion chamber. Here we find an effect of chemical regeneration of heat of the off-gas, an effect that was found for open cycles in [6-8]. However, the advantages of the cycle pass over into its disadvantages: Fuel combustion takes place over a wider interval of temperatures, and this is accompanied by considerable loss of exergy in spite of the favorable change in fuel composition; the lower potential of the heat that is taken off restricts the possibilities of its utilization in a binary cycle.

In the system with hydrogen takeoff, the chemical energy of the methane is transformed into three types of energy: work, chemical energy of hydrogen, and heat. The total exergetic value of the energy streams that are withdrawn is increased (this is expressed as an increase of η_e), mainly as a consequence of the lesser production of entropy in the combustion chamber (the temperature interval in which the combustion takes place is narrower); also, a certain positive effect is obtained from the change in ratio of CO and H_2 (the generation of entropy in the combustion of CO is somewhat lower). However, in characterizing the efficiency of the system as a whole, we must consider the differences in the true thermodynamic value of the individual components of the exergy. Thus, the real value of thermal exergy is always lower than that of electrical exergy. The situation is not so clear-cut in comparing the exergies of hydrogen and electricity. The real thermodynamic value of hydrogen for the manufacture of such extremely important chemical products as methanol (the most promising fuel of the next decade for transport [4]) or ammonia is even higher than the value of an equivalent quantity of electrical energy if it is taken

into account that the efficiency of water electrolysis is substantially less than unity. In this sense, electricity and hydrogen are actually mutually supplemental, universal energy carriers [1]. Therefore, the significant total increase of the quantity of electricity and hydrogen that are generated, expressed as the desired efficiency η , is the most important index of efficiency of the integrated system. Finally, an additional advantage of the cycle with hydrogen takeoff is the substantial increase in potential of the heat that is withdrawn; for example, the mean effective thermodynamic temperature of heat exchange in the section e/f is 722 K in comparison with 630 K for ef .

The most logical conversion of the application of hydrogen in the overall plan of the problems in energetics that we have discussed would be the utilization of hydrogen in an auxiliary cycle with superheating of steam by combustion of a hydrogen—oxygen mixture in the steam [9, 10]. When we consider that the potential of the heat withdrawn from the main cycle is sufficiently high for steam generation, the overall efficiency of the binary system with respect to electrical energy will be very high.

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